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SPATIAL CONCENTRATIONS OF SILICON ATOMS IN RF  
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R M ROTH ET AL. 18 FEB 85 TR-7 N00014-79-C-0622

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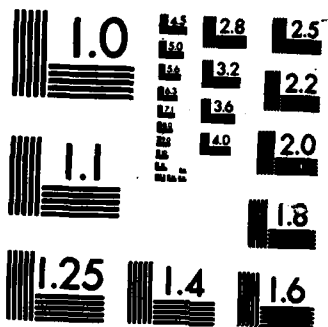
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# SPATIAL CONCENTRATIONS OF SILICON ATOMS IN RF DISCHARGES OF SILANE

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## ABSTRACT

A capacitively coupled rf glow discharge of silane in argon was studied to determine the spatial concentration of silicon atoms. Laser-induced fluorescence was used to determine the ground state concentration profiles. The fluorescence profiles clearly show the sharp boundaries of the sheath regions. The dc bias voltage, silane mole fractions, flow rates, and chamber pressure were all varied to establish the sensitivity of the silane profiles. The existing theory of sheath formation is used to qualitatively understand the existence of sharp spatial boundaries and the sensitivity of the anode sheath region to plasma chemistry.

## INTRODUCTION

The decomposition of silane in electrical discharges has been shown to form thin films of hydrogenated amorphous silicon on the electrodes. These films have promise for making inexpensive solid state devices, e.g., photovoltaics [1]. If the properties of the amorphous films are to be optimized, the chemical processes in the gas phase and at the gas-surface interface must be understood. Laser probes are well suited to the study of these gas phase chemical species because of their high spatial resolution, sensitivity, and the variety of different laser spectroscopic techniques available.

A frequently used discharge environment is a capacitively coupled rf glow discharge. In previous publications we have presented spatially resolved results from laser excited silicon atom fluorescence [2] and from particle light scattering [3] in a capacitively coupled rf glow discharge of silane and argon. In this article, we present results from recent experiments on the nature of our silicon atom fluorescence data. In the accompanying article [4], we discuss the nature of particle light scattering and its relation to the silicon atom fluorescence.

## EXPERIMENTAL

Our apparatus is designed to use laser probes with a discharge that has features and parameters typical of discharges used by other investigators to prepare amorphous silicon films [1]. Our laser system consists of a dye laser pumped by a pulsed Nd:YAG laser. The dye beam can be frequency doubled to produce a tunable UV beam. The laser system is operated at 10 Hz and produces light pulses 10 ns in duration with energies as high as a few millijoules in the visible, and a few tenths of millijoules in the UV.

The discharge chamber is pictured schematically in figure 1. The laser beam enters and exits the chamber through Brewster windows that are mounted perpendicular to the plane of the paper in figure 1. The laser



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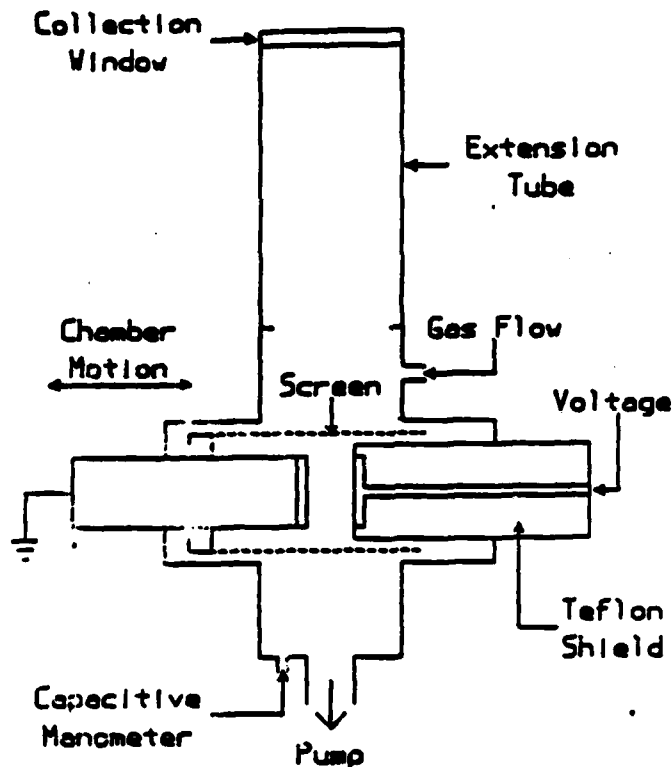


Figure 1 Schematic diagram of the discharge chamber. The laser entrance and exit ports are perpendicular to the plane of the figure.

focusing is done with a telescope lens pair mounted 0.5 m from the image spot size of 0.1-0.15 mm as determined from film burn patterns. The electrodes are 38 mm in diameter and separated by 22 mm. The rf electrode is shielded from the chamber, while the ground electrode is in mutual ground with the chamber. Thus, the effective area of the ground electrode is larger than the rf electrode. The signal is detected through a collection window mounted perpendicular to the laser ports. In order to prevent the formation of amorphous silicon films on the collection window and laser windows, a plasma constraining screen at ground potential is placed around the discharge area. A chamber extension tube, through which the silane mixture enters, is used to separate the collection window from the discharge region by both flow and distance.

The laser signal is detected by imaging the slit of a 0.75 m monochromator, through a lens pair of aperture f7.4, onto the laser beam. The signal from the exit slit of the monochromator is detected on a photomultiplier tube. A fast, gated integration of  $\sim 100$  ns provides digital signals to a microcomputer. The microcomputer controls the entire experiment, which allows efficient data collection and excellent signal averaging. The monochromator, the 10 ns pulse length, and gated detection all serve to discriminate against plasma emission. The apparatus is calibrated

by filling the chamber with 0.10 torr of benzene vapor and detecting the well known fluorescence spectrum [5] as a function of spatial position. High resolution spatial profiles along the axis of the electrodes are obtained by translating the vacuum chamber with respect to the fixed optics system (see figure 1). This alleviates the problems involved with retaining alignment while translating a laser beam. A flexible connection to the vacuum pump allows chamber motion, and the vacuum pump and chamber system holds a constant pressure to an accuracy of  $\sim 0.1\%$  by servo control of an argon leak between a particle trap and the pump.

Silicon atom fluorescence is detected by weakly focusing the UV laser beam into the discharge region. The laser wavelength of 251.43 nm excites ground state  $\text{Si}, 3p^2\ ^3P_0 \rightarrow 4s\ ^3P_1^o$  and fluorescence of the  $4s\ ^3P_1^o \rightarrow 3p^2\ ^3P_2$  transition at 252.85 nm is detected through the monochromator. The monochromator resolution of  $\sim 0.5$  nm cleanly separates the 252.85 nm emission from the excitation line and the other member of the triplet emission. This separation nearly reaches the base line and light scattering at the resonance excitation does not overlap the 252.85 nm peak. The conventional meaning of fluorescence, emission excited by optical absorption, is used in the following text. The more general excitation of emission, including by electrons, should not be called fluorescence. The recent common use of LIF, for laser induced fluorescence, is often misused because the laser induced is only needed when ambiguity might exist as to the type of optical excitation.

#### RESULTS AND DISCUSSION

When an rf discharge is created, ion sheaths form near both electrodes. Sharp boundaries suggestive of ion sheaths are clearly evident in the axial profiles of silicon atom fluorescence presented in figure 2. These curves show no electrode wall effects, as determined from the benzene experiments. In order to understand these spatial profiles, the discharge parameters were varied to probe both chemistry and electrical sheath behavior. As the total gas pressure was increased at constant silane mole fraction and discharge power, the intensity of the fluorescence signal increased, and the location of the peaks changed relative to the electrode. This increase of fluorescence intensity with pressure implies that the total atom concentration has a creation mechanism that depends on pressure. The movement of the fluorescence peaks closer to the electrode surface with increasing pressure is compatible with the theoretical concepts of ion sheath formation [6]. This model suggests that the product of pressure and sheath distance to the electrode should remain constant, and this is exactly what is observed for the location of silicon atom fluorescence peaks. The reason for the silicon atoms having boundaries at the sheaths is a key object of the current research report, although it is obvious that it is related to the atom creation mechanism. In our earlier report [2] we implied that the most probable cause was the onset of high electron energy creation processes from silane and silane fragments.

The mole fraction of silane in argon is shown in figure 2 to weakly affect both the shape and intensity of the silicon atom spatial profiles. The mole fractions of 2%, 6%, and 9% show an increasing atomic signal with decreasing mole fraction of silane. At these large mole fractions, one has difficulty separating the effects of atom creation mechanisms from changes in the discharge characteristics. It is clear, however that at some point there should be a reduction in atom intensity as one reduces the silane mole fraction. Furthermore, when one reaches the mole fraction where the electron distributions are controlled by the dominant argon concentration, the spatial profiles of atom concentration should reflect the electron distributions in the plasma and sheath regions by a convolution of electron

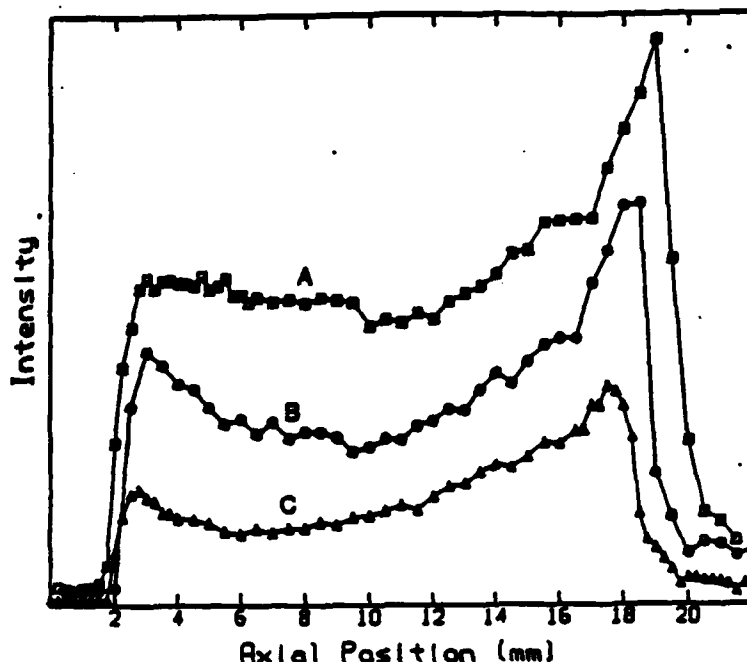


Figure 2 Axial profiles of atomic silicon fluorescence signals for different mole fractions of silane in argon: A - 2%, B - 6%, C - 9%. The other discharge parameters are: rf power 5W, gas flow 50 sccm, gas pressure 0.3 torr, and rf frequency 12 MHz. The ground electrode is at 0.0 mm. The rf electrode is at 22.0 mm.

impact and other creation mechanisms with silicon diffusion and loss processes. The normal model of a plasma suggests that a bulk plasma of fairly constant electron impact chemistry should be bordered by the ion sheaths, at which the transition in electron distributions and electron impact chemistry may show differences from the bulk plasma. Consequently, one might expect curves much like those shown in figure 2, but with smaller silicon atom signals for smaller mole fractions of silane. The silane is an important component in controlling the electron impact processes and changes from 2-9% are probably greatly affecting the electron processes and therefore the atom concentration. At smaller mole fractions we might expect to reach a perturbation limit, where the electron impact processes are largely controlled by argon. Figure 3 shows results from experiments performed at silane mole fractions between 0.05% and 0.45%. While it is not shown in figure 3, the change from 2.0% to 0.45% reduced the sharp cusp like behavior to a simple sharp boundary at 0.45%. This type of change from a cusp to a sharp edge might be expected on the basis of discharge changes involved in reaching a perturbation limit. The changes shown in figure 3 at lower mole fractions are not compatible with our expectation for the discharge electron impacts creating silicon atoms. In particular, at 0.2% one can observe a peak in silicon atom concentration at 3.5 mm, the original location of the sharp cusps that appear to correlate with the ion sheaths. In addition, the very low mole fractions of silane show changes with concentration that are not compatible with the concept of a reasonably

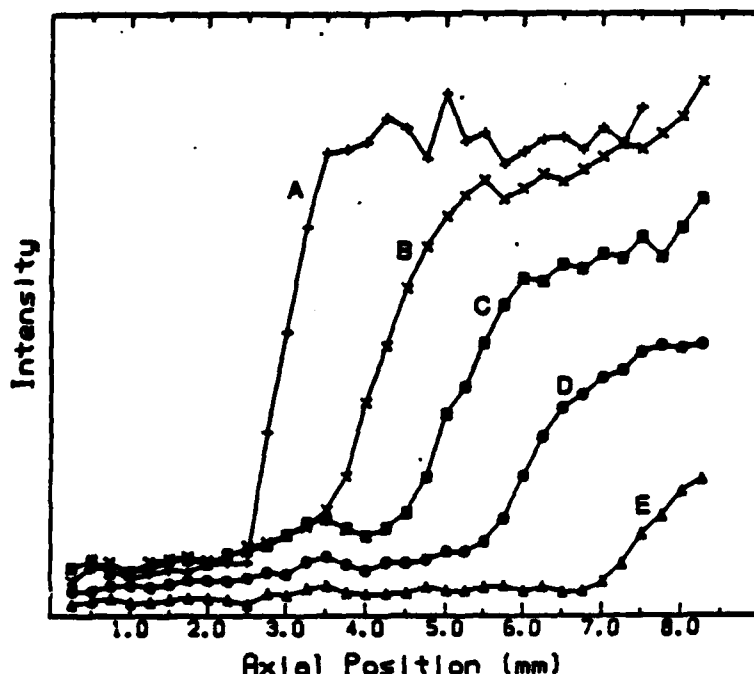


Figure 3 Axial profiles of atomic silicon fluorescence signals near the ground electrode (0.0 mm), for different mole fractions of silane in argon: A - 0.45%, B - 0.35%, C - 0.20%, D - 0.10%, E - 0.05%. The other discharge parameters are: rf power 3W, gas flow 50 sccm, gas pressure 0.5 torr, and rf frequency 12 MHz.

uniform plasma between sheaths that is only weakly perturbed by silane. However, the atom signals do reflect the discharge electrical characteristics by their spatial correlation with ion sheaths, especially at larger mole fractions of silane.

In order to further understand the origin of the silicon atom signals we have done a number of other experiments. From laser-induced fluorescence one can, in principle, obtain a quantitative measure of concentration. In our initial calibration experiments with benzene, we were able to conclude that the laser power which was necessary to see the fluorescence signal above the noise was far above that necessary to saturate the atomic transition. The resultant concentration of silicon atoms, in the case of saturation, is  $\sim 1 \times 10^9/\text{cc}$ , based on the absolute yield of the benzene emission and measurements of focus volume, line widths, and an unproven assumption of a simple saturation mechanism. However, the experimental test of saturation was contradicted by a linear dependence of fluorescence signal on laser power. The linear dependence had a non-zero intercept indicating some sort of power threshold, an observation that was difficult to understand. In our next effort to understand the laser power dependence of silicon atom fluorescence, an experiment was performed in which the focus diameter of the beam was expanded by about a factor of three to  $\sim 0.35$  mm. Additional focusing control and detection calibration must yet

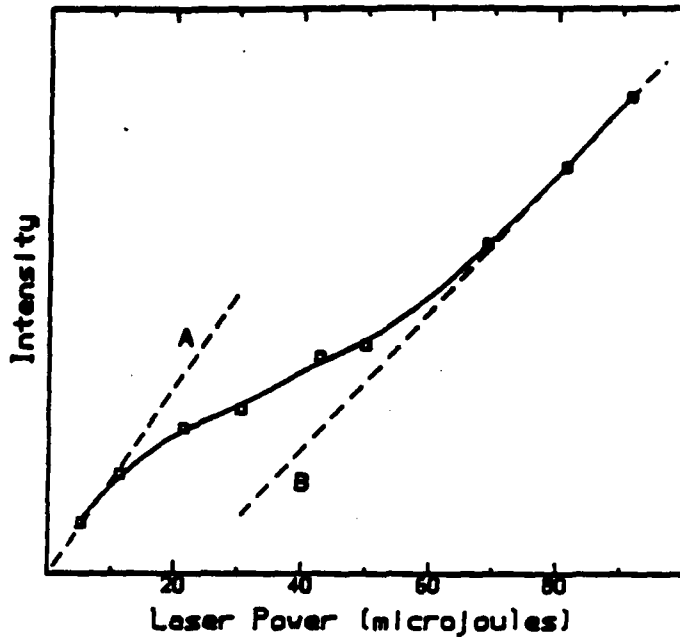


Figure 4 A plot of laser power versus fluorescence intensity. Line A represents non-saturation limit behavior. Line B represents a second high power mechanism.

be done to use the focusing volume changes in a quantitative manner and obtain an improved estimate of atom concentration. Nevertheless, the expanded area of the laser beam allows a more sensitive measurement of fluorescence signal versus laser power density. The resultant data are plotted in figure 4. Although the laser power for all the points in figure 4 are above the calculated saturation power, we can more clearly observe the onset of a linear power dependence. At low powers, the curvature of the plot is due to typical saturation rollover as seen by the deviation from a linear behavior (line A). As the power is increased, a second mechanism takes over which has a linear dependence on power with some threshold (line B). The new mechanism is compatible with laser excited creation of atoms from some species in the discharge. In order to study intrinsic silicon atom concentrations, much lower power densities will be needed than were used in this work. The necessity for a discharge, the spatial variation of silicon atom signal, and the intensity and spatial changes with mole fraction all suggest that particles are the species that are responsible for laser absorption and atom creation during the laser pulse. A new experiment is being planned that uses two laser beams of variable colors to probe the process of particle absorption and atom creation. Other data showing correlations with particle signals are shown in an accompanying paper [4].

In conclusion, we have shown that the observed spatial profiles of silicon atoms (2) are not derived from plasma chemistry in a direct manner. At sufficiently large laser powers, the atom concentrations are probably created by absorption of radiation by particles that exist in spatial zones controlled by the discharge properties and the discharge chemistry.

#### ACKNOWLEDGMENT

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